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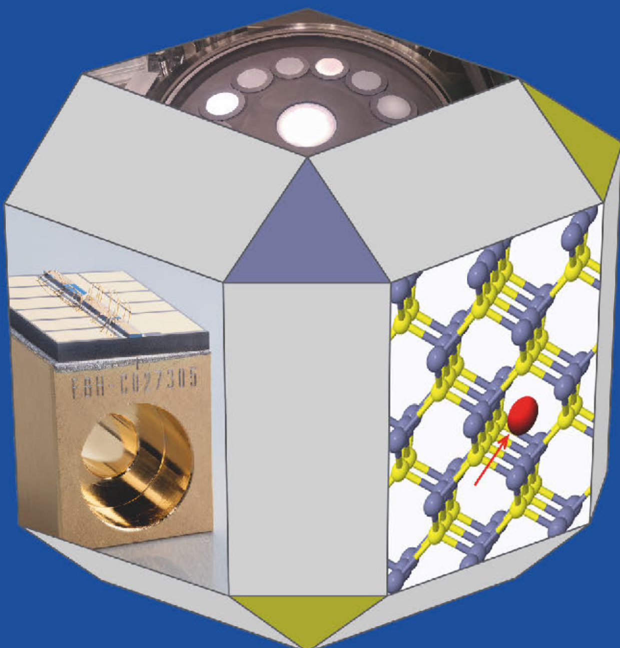
Innovationen mit Mikrowellen & Licht

Forschungsberichte aus dem
Ferdinand-Braun-Institut,
Leibniz-Institut
für Höchstfrequenztechnik

Two-step MOVPE, in-situ etching and buried implantation: applications to the realization of GaAs laser diodes



Pietro della Casa

aus der Reihe:

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Two-step MOVPE, in-situ etching and buried implantation: applications to the realization of GaAs laser diodes

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Innovations with Microwaves and Light

Research Reports from the Ferdinand-Braun-Institut, Leibniz-Institut für Höchstfrequenztechnik

Preface of the Editors

Research-based ideas, developments, and concepts are the basis of scientific progress and competitiveness, expanding human knowledge and being expressed technologically as inventions. The resulting innovative products and services eventually find their way into public life.

Accordingly, the *“Research Reports from the Ferdinand-Braun-Institut, Leibniz-Institut für Höchstfrequenztechnik”* series compile the institute’s latest research and developments. We would like to make our results broadly accessible and to stimulate further discussions, not least to enable as many of our developments as possible to enhance everyday life.

Broadly tunable laser diodes for measurement applications require multiple growth steps with intermediate patterned processing This is particularly challenging in the presence of Al in GaAs-based device heterostructures. Exposure of AlGaAs to atmosphere is avoided by protective GaAs or GaInP layers. In-situ etching inside of the growth reactor removes oxides as well as these protective layers and thus enables growth on a clean surface. Also, broad area laser diodes can benefit from such processes, leading to enhanced device efficiency. This thesis presents a toolbox of different processes, yielding buried heterostructures with excellent device performance for different applications. Hence, this modular approach paves the way for innovative GaAs-based laser diode concepts.

We wish you an informative and inspiring reading

Prof. Dr. Günther Tränkle
Scientific Director

Prof. Dr.-Ing. Wolfgang Heinrich
Scientific Deputy Director

The Ferdinand-Braun-Institut

The Ferdinand-Braun-Institut researches electronic and optical components, modules and systems based on compound semiconductors. These devices are key enablers that address the needs of today’s society in fields like communications, energy, health and mobility. Specifically, FBH develops light sources from the visible to the ultra-violet spectral range: high-power diode lasers with excellent beam quality, UV light sources and hybrid laser systems. Applications range from medical technology, high-precision metrology and sensors to optical communications in space and integrated quantum technology. In the field of microwaves, FBH develops high-efficiency multi-functional power amplifiers and millimeter wave frontends targeting energy-efficient mobile communications as well as car safety systems. In addition, compact atmospheric microwave plasma sources that operate with economic low-voltage drivers are fabricated for use in a variety of applications, such as the treatment of skin diseases.

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Two-step MOVPE, in-situ etching and buried implantation: applications to the realization of GaAs laser diodes

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Abstract

This work concerns the use of two-steps epitaxial growth, realized with metalorganic vapor-phase epitaxy (MOVPE), combined with in-situ etching and buried ion implantation, for the realization of GaAs-based edge emitting laser diodes, emitting in the near infrared region around 1 µm wavelength. The fabricated devices fall into two categories: tunable lasers (milliwatt range, monomodal) and high-power lasers (watt range, multimodal).

In the first case, the use of multi-step epitaxy is a *requisite*, and the task is that of making now this kind of process feasible with GaAs-based materials, similarly to what has been realized in the past with InP-based materials in the 1.3-1.5 µm wavelength range.

In the second case, a multi-step epitaxy is only an *option*, which can be exploited to introduce additional elements – as buried electrical and optical confinement structures – in the devices; a comparison of their performance and reliability with those of lasers fabricated with single epitaxy is then conducted to assess the effectiveness of this alternative approach.

Common for both cases is the requirement that surface contamination - particularly that due to oxygen - is removed before regrowth. This is more challenging than in the case of InP/GaInAsP structures, because here the ternary AlGaAs is used as cladding and waveguide material, and aluminum forms very strong bonds with oxygen. In turn, oxygen forms deep levels inside the bandgap which are effective non-radiative recombination centers.

Thus, in-situ etching with carbon tetrabromide (CBr_4) is first studied: the experimental results are presented, including kinetic data, the effects of different etching conditions and of the substrate characteristics on obtained morphology. Simple models are proposed to interpret the etching mechanism. Moreover, the utilization of the in-situ etching is discussed in relation to the reduction of residual surface contamination and enabling in-situ pattern transfer.

These investigations pave the way to devices based on 2-step epitaxy, combined with in-situ etching. The successful fabrication of thermally-tuned SG-DBR lasers operating around 975 nm is first described: a tuning range of 21 nm is demonstrated.

The possibility of using electronic injection for the tuning (which would allow a faster wavelength shift) is then explored, and the related issues discussed. It is suggested that fundamental material limitations confine the usable wavelength range to values lying near GaAs fundamental absorption edge at ≈ 870 nm. For wavelengths beyond 900 nm, the change in the refractive index that can be obtained in GaAs is too small, and there is no material option available which can be grown pseudomorphic to GaAs but with smaller bandgap.

High-power broad-area lasers have also been realized, using a two-step epitaxy combined with ex-situ + in-situ etching, to create a buried, shallow "mesa" containing the active zone. This approach allows introducing lateral electrical and optical confinement, and – simultaneously - non-absorbing mirrors at the laser facets.

This is reflected in performance and reliability improvements, but at the current state of development, the energy efficiency is still penalized by the two-step process with respect to a single epitaxy, because of additional non-radiative recombination paths. This is due to some extent to the additional etch-stop layers, needed for selective wet etching, that have to be added to the basic (and optimized) layer structure grown without intermediate patterning. Presently, the advantage of the lateral confinement appears to overcome the extra losses when the width of the lasers is below approximately 30 µm. Optimization of the heterostructure may further reduce the losses, making this strategy interesting even for larger devices.

Finally, a different strategy to create deep lateral current confinement in broad-area lasers, based on ion implantation *followed* by epitaxial regrowth, is presented. Two variants, differing in the position of ion

implantation with respect to the active zone, are compared. While implantation into the waveguide introduces issues related to increased non-radiative recombination and optical losses, implantation into the p-cladding allows the improvement of device performance and the simultaneous introduction of non-absorbing mirrors at the facets, with corresponding improvement of the reliability. Here no pre-regrowth patterning through selective wet-etching is required and no etch-stop layers are inserted, so that the optimized layer sequence can be used. Thus, this approach represents a straightforward means to improve the performance of high-power broad-area devices.

In summary, this work has thus evaluated a “tool box” allowing different approaches towards the realization - within GaAs-based structures - of buried functional elements: *electrical* (current injection aperture) or *optical* (gratings, lateral optical confinement, butt-coupled active/passive sections, non-absorbing mirrors). Based on this knowledge, new devices are enabled (*GaAs* widely-tunable SG-DBRs) or new approaches towards improved device characteristics (high-power lasers) are opened up. However, the advantageous features that can be introduced with processes based on two epitaxial growth steps coexist with penalties associated to residual regrowth interface defectivity and to the modifications introduced in the vertical structure in order to allow the intermediate ex-situ processing. A favorable trade-off between these two aspects has to be sought.

Particularly for buried implantation such a good compromise has already been found. A reduction of threshold current by ≈12% and ≈15% increase of slope efficiency with respect to standard lasers with comparable processing and design has been obtained by implantation of oxygen, with a dose of 10^{15} cm^{-2} at 250 keV into the AlGaAs p-cladding layer and subsequent regrowth of the p-GaAs contact layer.

Kurzfassung

Diese Arbeit behandelt die Verwendung von zweistufigen Epitaxieprozessen, realisiert mit metallorganischer Gasphasenepitaxie (MOVPE), kombiniert mit in-situ-Ätzen und vergrabener Ionenimplantation, für die Realisierung von GaAs-basierten kantenemittierenden Laserdioden, die im nahen Infrarotbereich um ≈1 µm Wellenlänge emittieren. Die hergestellten Bauelemente lassen sich in zwei Kategorien einteilen: abstimmbare Laser (Milliwatt-Bereich, monomodal) und Hochleistungslaser (Watt-Bereich, multimodal).

Im ersten Fall ist der Einsatz von mehrstufiger-Epitaxie eine *Voraussetzung* für die Realisierung der entsprechenden Bauelemente. Die Aufgabe besteht darin, solche Prozesse auch mit GaAs-basierten Materialien möglich zu machen, ähnlich wie sie bisher mit InP-basierten Materialien im Wellenlängenbereich von 1,3-1,5 µm realisiert werden.

Im zweiten Fall ist eine mehrstufige Epitaxie nur eine *Option*, die genutzt werden kann, um zusätzliche Elemente – wie vergrabene elektrische und optische Einschlussstrukturen – in die Bauelemente einzubringen. Um die Effektivität dieses alternativen Ansatzes zu ermitteln, ist ein Vergleich der Leistung und Zuverlässigkeit solcher Bauelemente mit denen von in nur einem Epitaxieschritt hergestellten Lasern erforderlich.

Gemeinsam ist in beiden Fällen die Forderung, dass die Kontamination der Oberfläche - insbesondere durch Sauerstoff - vor dem Wachstum entfernt werden muss. Dies ist anspruchsvoller als bei InP/GaInAsP-Strukturen, da hier das ternäre AlGaAs als Material für Wellenleiter- und Mantelschicht verwendet wird und Aluminium sehr starke Bindungen mit Sauerstoff bildet; Sauerstoff wiederum bildet im Halbleiter tiefe Störstellen innerhalb der Bandlücke, die effektive nicht-strahlende Rekombinationszentren sind.

Deswegen wird zunächst das in-situ Ätzen mit Tetrabromkohlenstoff (CBr_4) untersucht: die experimentellen Ergebnisse werden vorgestellt, einschließlich kinetischer Daten und der Auswirkungen verschiedener Ätzbedingungen und der Substrateigenschaften auf die erhaltene Morphologie. Einfache Modelle werden vorgeschlagen, um den Ätzmechanismus zu interpretieren. Darüber hinaus wird der Einsatz des in-situ Ätzens im Zusammenhang mit der Verringerung der Oberflächen Restkontamination und der Ermöglichung der in-situ Musterübertragung diskutiert.

Die Untersuchungen zum in-situ Ätzen ebnen den Weg zu Bauelementen, die auf 2-stufiger Epitaxie, kombiniert mit in-situ Ätzen, basieren. Die erfolgreiche Herstellung von thermisch abgestimmten SG-DBR Lasern mit einem Arbeitsbereich um 975 nm wird zunächst beschrieben: ein Abstimmbereich von 21 nm wird demonstriert.

Anschließend wird die Möglichkeit der Verwendung elektronischer Injektion für die Abstimmung (was eine schnellere Wellenlängenverschiebung ermöglichen würde) untersucht. Es stellte sich heraus, dass grundlegende Materialbeschränkungen den nutzbaren Wellenlängenbereich auf Werte beschränken, die nahe der fundamentalen Absorptionskante von GaAs bei ≈ 870 nm liegen. Für Wellenlängen jenseits von 900 nm ist die in GaAs über Ladungsträgerinjektion erzielbare Änderung des Brechungsindex zu gering. und es gibt keine Materialoption, die pseudomorph zu GaAs ist, aber eine kleinere Bandlücke hat.

Hochleistung-Breitstreifenlasern wurden ebenfalls realisiert, wobei eine zweistufige Epitaxie in Verbindung mit ex-situ + in-situ Ätzen verwendet wurde, um eine vergrabene, flache «Mesa» zu erzeugen, die die aktive Zone umfasst. Dieser Ansatz ermöglicht die Einführung eines lateralen elektrischen und optischen Einschlusses und gleichzeitig nicht-absorbierenden Spiegeln an den Laserfacetten.

Dies spiegelt sich in Leistungs- und Zuverlässigkeitsverbesserungen wider, aber beim aktuellen Entwicklungsstand wird die Energieeffizienz immer noch durch das zweistufige Verfahren im Vergleich zu Wachstum in einem einzigen Schritt aufgrund zusätzlicher nichtstrahlender Rekombinationswege beeinträchtigt. Dies liegt zum Teil an den zusätzlichen Ätzstopp-Schichten, die für das selektive Nassätzverfahren benötigt werden, die zur (optimierten) ursprünglichen Schicht-Struktur ohne

Zwischenprozessierung hinzugefügt werden müssen. Gegenwärtig scheint der Vorteil des lateralen Einschlusses die zusätzlichen Verluste zu überwiegen, wenn die Breite der Laser unterhalb von ca. 30 µm liegt; eine Optimierung der Heterostruktur kann die Verluste weiter verringern, was diese Strategie auch für breitere Bauelemente interessant macht.

Schließlich wird eine andere Strategie zur Schaffung eines tiefen lateralen Stromeinschlusses in Breitstreifenlasern vorgestellt, die auf Ionenimplantation mit anschließendem epitaktischem Überwachsen basiert. Es werden zwei Varianten verglichen, die sich hinsichtlich der Position der Ionenimplantation in Bezug auf die aktive Zone unterscheiden: während die Implantation in die Wellenleiterschicht Probleme im Zusammenhang mit erhöhter nicht-strahlender Rekombination und optischer Verluste aufwirft, ermöglicht die Implantation in die p-Mantelschicht eine Verbesserung der Ausgangsleistung und die gleichzeitige Einführung nicht-absorbierender Spiegel an den Facetten mit einer entsprechenden Erhöhung der Zuverlässigkeit. Hier ist keine Vorwachstumsstrukturierung durch selektives Nassätzen erforderlich und es werden keine Ätzstopp Schichten eingefügt, sodass die optimierten Schichtenfolgen genutzt werden können. Dieser Ansatz stellt somit einen einfachen Weg dar, die Leistungsfähigkeit von Hochleistungs-Breitstreifenlasern zu verbessern.

Im Rahmen dieser Arbeit wurde damit ein «Werkzeugkasten» evaluiert, der unterschiedliche Ansätze zur Realisierung von vergrabenen *elektrischen* (Apertur für die Strominjektion) oder *optischen* (Gitter, lateraler optischer Einschluss, butt-coupled aktive/passive Sektionen, nicht-absorbierende Spiegel) *Funktionselementen* innerhalb von GaAs-Strukturen erlaubt. Basierend auf diesen Erkenntnissen werden neue Lasern (weit-abstimmbare *GaAs* SG-DBR) oder neue Ansätze zur Verbesserung der Lasereigenschaften (Hochleistungslasern) ermöglicht.

Den vorteilhaften Funktionen, die mit den entwickelten, auf zwei epitaktischen Wachstumsschritten basierenden Verfahren eingeführt werden können, , stehen jedoch Nachteile gegenüber, die mit an der überwachsenen Grenzfläche und den für die ex-situ Zwischenprozessierung nötigen Modifikationen der vertikalen Struktur verbunden sind. Daher muss immer ein geeigneter Kompromiss zwischen diesen beiden Aspekten gefunden werden.

Insbesondere für die vergrabene Implantation wurde ein solcher Kompromiss bereits gefunden. Durch die Implantation von Sauerstoff mit einer Dosis von 10^{15} cm^{-2} bei 250 keV in die AlGaAs p Mantelschicht und anschließendem Überwachsen mit der p-GaAs-Kontaktschicht wurde eine Reduktion des Schwellenstroms um ≈12% und eine Steigerung der differentiellen Effizienz (Steilheit) von ≈15% gegenüber Standardlasern mit vergleichbarem vertikalen Aufbau und gleicher Prozessierung erreicht.

Acknowledgments

The opportunity to work in the stimulating environment of the Ferdinand-Braun-Institut has been given to me by Prof. Dr. Günther Tränkle, who I wholeheartedly thank for his trust.

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I cannot recollect a single member of the material technology team to whom I do not owe some help, suggestion or constructive discussion; my thanks also go to all of them.

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Dr. Karl Häusler has contributed to the investigation concerning the buried-implanted lasers, coordinating the characterization of mounted devices and the reliability tests. Tim Adam and Christian Goerke have analyzed some of these devices in the framework of their Master's theses, and selected results from the latter concerning beam quality are summarized in chapter 7 (section 7.6.2).

The characterization of the mounted buried-mesa lasers has been supervised by Dr. Jonathan Decker and Dr. Martin Winterfeldt, and has been carried out with the aid of Alexander Putz and Lukas Hadasch.

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Finally, Dr. Hans Wenzel has provided the WIAS-TeSCA simulations, and has been in general a reference point for all the discussions regarding the device physics.

Contents

1 Introduction

This work concerns the use of two-steps epitaxial growth, realized with metalorganic vapor-phase epitaxy (MOVPE), combined with in-situ etching and buried ion implantation, for the realization of GaAs-based edge emitting laser diodes. The fabricated devices fall into two categories: high-power lasers (watt range, multimodal) and tunable lasers (milliwatt range, monomodal).

The experimental work encompasses different investigations, which were in part aimed to get a better understanding of potentials and limitations of the manufacturing technologies - ideally defining some transferrable "building blocks" for device fabrication - and in part more focused on characteristics and performance of the specific devices.

Although a particular emphasis is given to the material-related topics, different aspects – processing, device design and characterization – are often combined in the exposition, as they were in the actual project developments.

The intent of the author is that of presenting the more significant challenges and questions arisen in the various part of the work as "open problems", and to discuss the possible answers, in the belief that the merit and interest of the exposed material lies essentially in this critical process of understanding.

Chapters content

Chapter 2 contains a short, introductory description of III-V Zincblende semiconductors: their main crystalline characteristics, the effect of added or unwanted impurities, their relevance for the realization of optoelectronic devices. A broader – although still very condensed – description of the properties of III-V semiconductors is provided as foundation material appendix 1.

Chapter 3 presents the MOVPE technology, focusing on the epitaxial reactors and the set of reagents used in this work. A more in-depth discussion of several aspects of the MOVPE process can be found in appendix 2.

In **chapter 4** the in-situ etching with carbon tetrabromide (CBr_4) is studied: the experimental results are presented, including kinetic data, the effects of different etching conditions and of the substrate characteristics. Simple models are proposed to interpret the etching mechanism. Moreover, the possible usefulness of the in-situ etching is discussed, in particular in relation to the problems of reducing surface contamination and enabling in-situ pattern transfer. The in-situ etching has been used in the investigations presented in the following three chapters.

Chapter 5 deals with the realization of widely-tunable sampled-grating distributed Bragg reflector lasers (SG-DBR). After a general description of the working principle of these devices, the technological aspects of their realization – in particular in relation to the 2-step epitaxy - are presented. Two approaches to the tuning are compared, thermal and electronic. Only the first has led to the realization of working devices, and the reasons behind the difficulties encountered with the second approach are discussed. Fig. 1.1 represents schematically the different sections of the realized SG-DBRs.

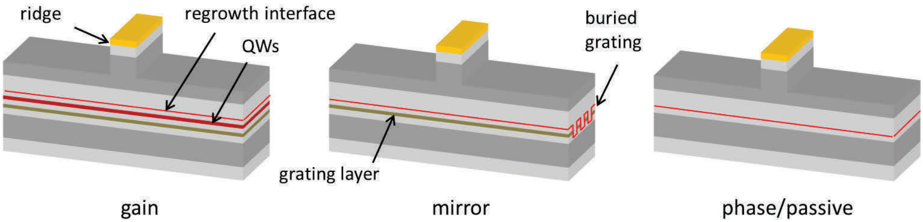

Figure 1.1 Schematic of the different sections of SG-DBR lasers of chapter 5.

Chapter 6 describes the realization of high-power broad-area lasers (BAL), using a two-step epitaxy process to create a buried, shallow "mesa", containing the active zone; the approach allows introducing lateral electrical and optical confinement, and simultaneously non-absorbing mirrors (NAM) at the laser facets (Fig. 1.2). Device results are presented and process limitations are discussed.

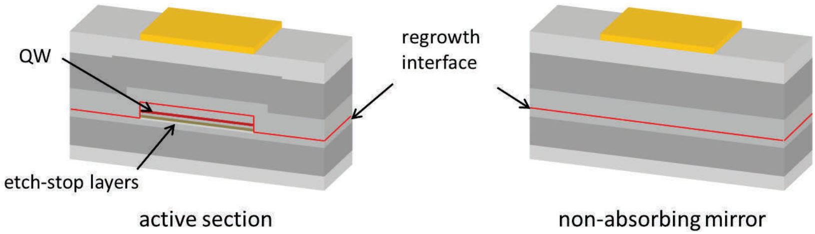

Figure 1.2 Active and passive (NAM) sections of the buried-mesa BALs of chapter 6.

Chapter 7 presents a different strategy to create deep lateral current confinement in BALs, based on ion implantation *followed* by epitaxial regrowth. Two approaches are compared, one more conservative, where the implantation is done in the upper cladding and the regrowth interface is in a "safe" position (it cannot cause non-radiative recombination) and one more challenging, with the implantation and the regrowth interface both in the waveguide layers (Fig. 1.3). While the first approach has given positive results in term of device performance, the second has proved more problematic; results and possible lessons learned are discussed.

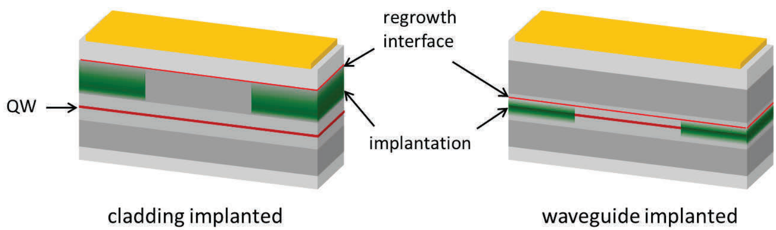

Figure 1.3 Two different positions of implantation and regrowth interface in BALs of chapter 7.

2 Zincblende III-V semiconductors

2.1 Chapter introduction

This chapter briefly introduces III-V semiconductors, with focus on those that have the same crystal structure of GaAs (Zincblende); only a very few aspects are rapidly touched, selected in an effort to provide a minimal material-related background relevant to the experimental part, without encumbering the narrative with an excessive amount of literature-based information.

Nonetheless, a quite broader – although still extremely condensed - discussion of III-V semiconductors' structural, electrical and optical properties, especially those that are more relevant to the realization of optoelectronic devices, is presented as "foundation material" - and possibly useful reference - in Appendix 1.

2.2 Zincblende crystal structure

III-V compounds having As, P and Sb as group V elements crystallize preferably in the Zincblende structure [1].

Within the crystal, each atom has four nearest neighbors of the other species, arranged in a tetrahedron, and the bonding can be interpreted in terms of valence bond theory assuming sp^3 hybridization of both species with formation of four localized sigma bonds, having an ideal angle of 109.47° between each pair.

In Zincblende there are 3 lowest-index high-symmetry families of planes: {100}, {110} and {111}. Figure 2.1 shows a schematic of the corresponding crystal facets and views of atoms and bonds in the crystal, each taken from a direction normal to one of the facets.

The significance of these planes is not only related to symmetry properties but even to chemical reactivity and thermodynamic stability.

Impurity incorporation probability – during the epitaxial growth - can be different between different surfaces. Also the different bonding on different adjacent surfaces can result in different surface diffusion of the atomic species; this is the case for Al and Ga during the growth of the ternary AlGaAs over a patterned surface, resulting in compositional modulation, with zones having a higher or lower Al content. This is generally an unwanted effect in many practical applications, as for example when a ternary or quaternary compound is used for the regrowth over the mesa structure of buried-mesa laser devices, or over the etched Bragg grating in distributed feedback lasers (DFB) and distributed Bragg reflector lasers (DBR), because the compositional perturbation is difficult to control and can even facilitate the formation of extended defects at the conjunction of two growth fronts.

Under surface-reaction-limited conditions, growth and etch rates exhibit selectivity with respect to crystal facets. In the case of growth, the slowest-growing facets emerge over convex substrate geometries, and the fastest-growing facets in the concave; in the case of etch, the situation is reversed, the slowest-etching facets are revealed in concave geometries, the fastest-etching facets over convex geometries. The kinetically more inert faces (slow growth or slow etch) are typically parallel to (111) planes.

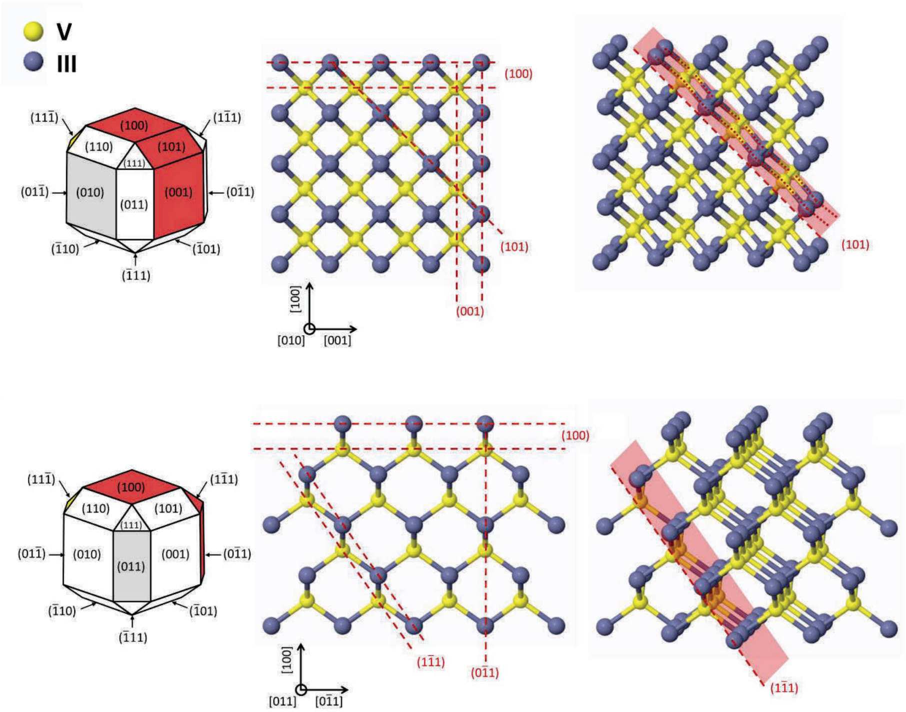

Figure 2.1 Zincblende lowest-index facets and corresponding views of the crystal. The facets in grey are normal to the observation direction, those in red are parallel. The dashed red lines indicate crystal planes perpendicular to the direction of observation. Rightmost, a small twist has been added with respect to the normal view.

The Zincblende Bravais lattice belongs to space group $F\bar{4}3m$ in Hermann-Mauguin notation (T_d^2 Schoenflies); it is symmorphic[1] and contains 24 point symmetry operations [2]. It does not include an inversion center, a characteristic that allows the onset of an electric field in consequence of the application of strain, because this can shift anions and cations in opposite directions (piezoelectricity). Although Zincblende contains directions, as the <111> and <100> along which anions and cations are alternated, the unstrained bulk Zincblende crystal has no net polarization because of its overall symmetry.

The {100} planes are perpendicular to the three 4-fold rotoreflection axes and three 2-fold rotation axis of the space group. Along a [100] direction, there is an alternation of group III and of group V layers: cleavage of the crystal parallel to one (100) plane leaves a facet terminated either with group III or group V atoms, in both cases with 2 dangling bonds for each atom. Addition or removal of a single atom

[1] A space group is symmorphic when there is a point such that all symmetry operations are the product of a symmetry operation which keeps this point fixed and a translation.

to/from a (100) surface involves no change in the number of dangling bonds. Most commonly, the semiconductor wafers used for device fabrication have a (100) upper surface.

The {110} planes are parallel to the six reflection planes of the space group, the ideal dihedral angle with {100} planes are 45° and 90°. Cleavage parallel to a (110) plane leaves on the surface group III and group V atoms in equal number, with one dangling bond for each atom; within the plane, the atoms are arranged in zigzag chains of consecutively bonded atoms. The cleavage along a (110) plane is facilitated by the absence of polarity in the [110] direction, a characteristic useful for the separation of discrete devices fabricated on (100) oriented wafers, especially when the facets must have optical quality as in the case of edge emitting lasers. Another characteristic, interesting in relation to edge emitter lasers reliability, is that – at least in the case of GaAs - no midgap surface states are expected to be present in ideally cleaved, relaxed (110) surfaces in absence of any oxidation or contamination [3].

The {111} planes are perpendicular to the four 3-fold rotation axes of the space group, the ideal dihedral angle between {111} and {100} planes is 54.74°, ½ of the tetrahedral bond angle. The {111} planes can be seen as a arranged in double layers, each consisting of two closely spaced planes, one containing only group III and the other only group V atoms, with each atom of one layer bonded to 3 of the other layer. These planes are designated with the letters A and B or with the atomic symbols, for example in the case of GaAs $\{111\}_A \equiv \{111\}_{Ga}$ and $\{111\}_B \equiv \{111\}_{As}$. A cleavage parallel to {111} between the A and B planes of a closely-spaced double layer would leave on the surfaces 3 dangling bonds for each atom, while a cleavage parallel to {111} between A and B planes belonging to consecutive double layers would leave only a single dangling bond for each atom.

When the *facet* of a crystal corresponds to a (111) plane, it is designated A or B according to which kind of atom layer *can* terminate the crystal with only *one* dangling bond per atom, assuming the more energetically stable termination: note that in this case, if each atom retains its own electrons, the group V atoms on a type-B facet will have two electrons per dangling bond while the group III atoms on a type-A facet will have no electrons in the dangling bonds[2]. The $\{111\}_A$ facets are usually the most kinetically stable with respect to chemical etching. The different facets are depicted in Fig. 2.2 along with a representation of a (100) wafer with orientation flats, according to the European-Japanese (E-J) convention.

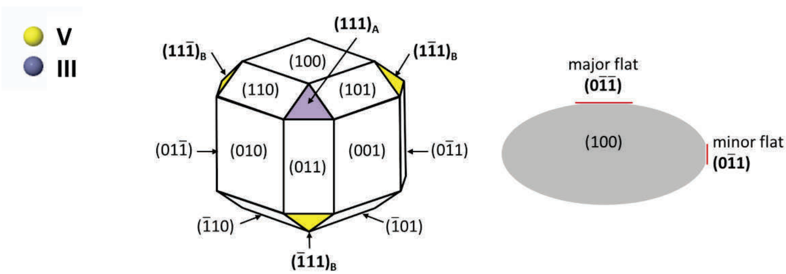

Figure 2.2 Left: $(111)_A$ and $(111)_B$ facets of Zincblende crystal; right:, wafer surface and flat orientation, according to E-J convention.

[2] This is not entirely accurate, because the dangling bonds of a non-reconstructed, neutral (111) surface are expected to bear a fractional charge (Appendix 1).

2.3 Point defects in III-V semiconductors

Defects related to the presence of foreign atoms are referred to as extrinsic defects. Defects that represent deviations from the regular arrangement of the lattice but are not associated to foreign atoms are called intrinsic.

Among the possible criteria for defects classification, one is based on dimensionality, and divides them into zero-dimensional - or point - defects and extended (1- 2- 3- dimensional). The presence of extended defects is in general unwanted in practical applications; their description goes beyond the scope of this chapter, but basic information has been included in Appendix 1. Point defects [4, 5] are not necessarily detrimental: they contribute in a fundamental way in determining the electrical and optical functionality of semiconductor materials and, moreover, they play a key role in diffusion processes and in device degradation processes.

In semiconductors, the electrons primarily involved in the optical and electrical processes relevant to optoelectronic devices, are those belonging to two separate sets of energetically finely-spaced levels, the valence band (VB) and the conduction band (CB); the difference between the lowest energy level of the CB and the highest energy level of the VB is called bandgap. Electrons in the CB are responsible for n-type conductivity (n-carriers), while empty electronic states (or holes) in the VB are responsible for p-type conductivity (p-carriers).

Electrically active defects introduce one or more energy levels within the bandgap, whose associated electronic wavefunctions are localized. Electrons can be exchanged between these localized levels and the bands.

Shallow electronic levels are those whose energy lies near the bottom of the CB or the top of the VB; usually this is intended in the sense that the difference between the level and the nearest band edge is less than the thermal energy k_BT (26 meV at 300 K). Occupied levels lying near the CB can be easily ionized, promoting electrons into the CB and are called donors; similarly unoccupied levels near the VB can easily accept electrons from the VB, leaving behind a hole, and are called acceptors. The (small) ionization energy of the donors and acceptor makes the electrical conduction an activated process.

Deep electronic levels have energies more near the center of the bandgap, with a stronger localization of the electrons (down to the size of an interatomic bond length). The corresponding defects are called deep defects. Some of them are effective electron-traps and/or hole-traps, in the sense that they can capture electrons from the CB or donate electrons to the VB, with the following effects: reduction of carrier density, reduction of carrier mobility via ionized defect formation and increase of non-radiative carrier recombination.

Foreign atoms creating donor or acceptor levels are called dopants; the range of *intentional* doping concentration spans several orders of magnitude, approximately from 0.1 to 1000 ppm. Dopant atoms for III-V semiconductors come usually from the neighboring groups II, IV and VI. They are incorporated in the crystal in the sites normally occupied by a group III or a group V atom, so that the number of the valence electrons of the impurity is higher or lower than that normally contributed by a constituent atom in that lattice position: p doping is obtained decreasing the number of electrons with II→III or IV→V substitutions, n doping increasing it with IV→III or VI→V substitutions. Concerning the specific selection of dopants species:

- VI→V substitution: S, Se and Te all introduce shallow donor levels; O introduces deep levels and cannot be used as a dopant.
- II→III substitutions: Be, Mg (group IIa) Zn and Cd (group IIb), introduce shallow acceptor levels; the other group II elements have not been used successfully for p-doping.
- IV→III and IV→V substitutions: group IV elements are electrically amphoteric, since they can be simultaneously incorporated in both III and V sublattices, leading to opposite kind of doping. The actual behavior depends on the specific material and from the doping process conditions. In GaAs, C is prevalently incorporated in the group V sites and is a shallow acceptor, Si is incorporated

prevalently in the group III sites where behaves as a shallow donor, Ge is strongly amphoteric, Sn is prevalently a shallow donor.

Silicon, carbon and zinc have been used as dopants in the experimental part of this work, while oxygen has been used to deliberately introduce deep levels.

2.4 III-V semiconductors and optoelectronics

III-V semiconductors as GaAs and InP are used in high-speed electronics applications, where their characteristics – in particular higher electron mobility and peak saturation velocity - make them superior to the otherwise more utilized silicon. In the framework of *opto*electronics, there are two fundamental reasons for their success: first, many of them are efficient light emitters, and second, it is technologically possible to monolithically integrate different material compositions having distinct electrical and optical properties.

The electrons can be excited, in particular by means of current injection or photon absorption, from the – largely occupied – valence band to the – largely empty – conduction band; the reverse disexcitation process can occur through different mechanisms, radiative (photon emission) or non-radiative. Efficient photon emitters are those semiconductors where the photon emission corresponding to the electronic transition from the lowest-energy states of the CB to the highest-energy states of the VB is possible without requiring a change in the momentum (or more properly in the *crystal* momentum) of the electrons. These transitions are called direct, and the semiconductors whose electronic band structure allows such transitions – as is the case for GaAs, InP and many other III-Vs, but not for Si - are called direct semiconductors. Under high-excitation conditions, which are relevant for laser devices, the total recombination rate of a bulk semiconductor (not including stimulated photon emission) is often expressed with the approximate "ABC equation":

$$R_{tot} = An + Bn^2 + Cn^3, \qquad \text{E1.1}$$

where n is the CB electron density; the first term represents the non-radiative recombination caused by the presence of deep levels, the second the (spontaneous) radiative recombination and the third the non-radiative recombination related to carrier-carrier scattering processes (Auger). In a direct semiconductor, the B coefficient is orders of magnitudes larger than in an indirect one. Of the three coefficients in E1.1, B and C stem from the fundamental properties of the material, while A depends on the kind and density of the defects, and is consequently the only one impacted by the material *quality*.

The monolithic integration of different III-V material compositions in a multilayered, epitaxial crystal structure is fundamentally limited by the necessity to guarantee similar average interatomic distances, or equivalently a similar lattice parameter, in order to avoid the formation of extended defects. Since for technological reasons the available bulk-grown substrates correspond to the binary compounds, the constraint is essentially that of combining the different atomic species, each of them characterized by a different size, in such a proportion that the resulting lattice parameter does not differ too much from that of the substrate, leading to "families" of devices indicated for example as "GaAs-based" or "InP-based". This leaves anyway a considerable room for the engineering of the material properties.

In the epitaxial growth of a multilayer stack, the transition between different materials can be a technologically critical point, because formation of defects or interlayers with undesirable composition might occur.

Once a laser is realized and tested, the task of determining to which extent the quality of the material and interfaces do actually condition its performance and reliability is – in many cases – not trivial; this will be an important topic in the following parts of the thesis.

3 MOVPE growth of III-V compounds

3.1 Introductory remarks on the MOVPE technique [6]

Epitaxy is the process of growing a crystalline material layer on a crystalline substrate, with the layer conforming to the lattice structure of the substrate. It is called homoepitaxy when substrate and layer materials are identical[1] and heteroepitaxy otherwise. Epitaxy is called pseudomorphic when any mismatch between the lattice parameters of the layer and of the substrate is elastically accommodated.

Metalorganic vapor phase epitaxy (MOVPE, also known as metalorganic chemical vapor deposition MOCVD) is the most widespread production method for the realization of light-emitting compound semiconductor devices.

In the MOVPE technique the reagents (or "precursors") are typically volatile metalorganic compounds (MO) and hydrides, which are transported in the deposition chamber highly diluted in a carrier gas, in most cases hydrogen. The chamber pressure can vary approximately in the range 10 to 1000 mbar, with values between 50 and 150 mbar more commonly used; carrier gas and precursors are kept under laminar flow conditions. The substrates are positioned on a rotating graphite susceptor, whose temperature depends on the material to be grown, and is in the range 550°C-850°C for III-V arsenides and phosphides, while higher temperatures are used for nitrides and lower temperatures for antimonides. Group III precursors are always introduced in lower amount than those of group V, and the growth rate is normally controlled by the diffusion of group III precursors from the gas phase to the substrate; the rate can reach typically some µm/h.

The technique is extremely flexible in terms of achievable material compositions, and allows good control over layer thickness, typically in the order of 2% for thick layers (i.e. approximately above 50 nm). Abrupt interfaces between layers of different composition can be obtained: with properly optimized switching sequences, the transition regions can be reduced to the monolayer range. This makes possible the realization of well-defined nanometer size structures, as needed in modern quantum-well lasers.

The experiments described in the present work have been conducted using MOVPE reactors produced by Aixtron SE, of a particular type called *planetary*; two different models were used, AIX2400G3 and AIX2800G4 (abbreviated in the following to **G3** and **G4**). Reactors and precursors are briefly described in the next sections. A more general description of MOVPE can be found in appendix 2.

[1] Alternatively, depending on the context, the terms homoepitaxy/heteroepitaxy are used to indicate that substrate and grown layer have/don´t have the same crystal structure.